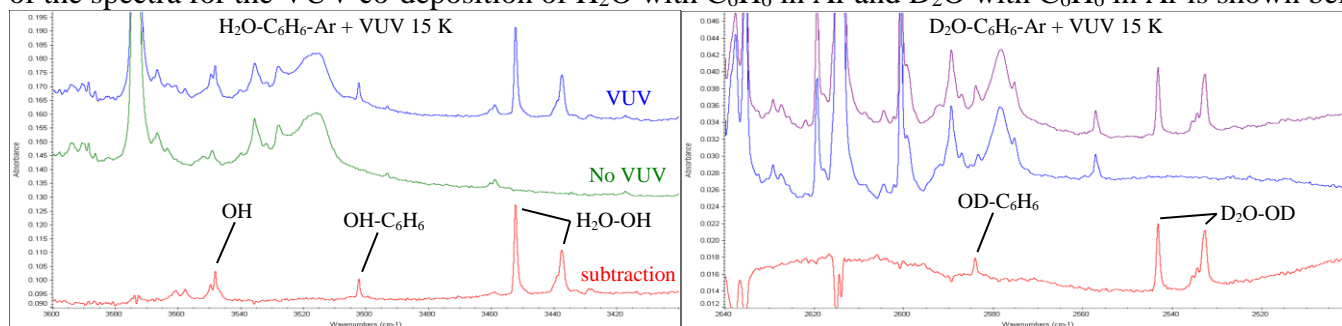


At the time of the last report period, I had three undergraduate students working in my research laboratory and we were performing experiments to observe the OH-C<sub>6</sub>H<sub>6</sub> radical complex in an Ar matrix. This radical complex has previously observed (*Ang. Chem. Int. Ed.* **2009**, *48*, 4804) using flash vacuum pyrolysis of azobenzene at 500 °C to produce the phenyl radical and co-depositing with H<sub>2</sub>O in an Ar matrix, then UV irradiation to produce the OH-C<sub>6</sub>H<sub>6</sub> radical complex. The O-H stretch of the OH-C<sub>6</sub>H<sub>6</sub> radical complex was reported at 3502.2 cm<sup>-1</sup> in Ar. We were able to produce the OH-C<sub>6</sub>H<sub>6</sub> radical complex Ar at 15 K in my lab by co-depositing H<sub>2</sub>O with C<sub>6</sub>H<sub>6</sub> while simultaneously irradiating with a vacuum-ultraviolet (VUV) photolysis source. We also observed the OH radical and the H<sub>2</sub>O-OH complex as well. After completing the H<sub>2</sub>O-C<sub>6</sub>H<sub>6</sub>-Ar + VUV experiments, we performed a series of D<sub>2</sub>O-C<sub>6</sub>H<sub>6</sub>-Ar + VUV experiments and were able to observe a peak at 2584.1 cm<sup>-1</sup> that is due to the OD-C<sub>6</sub>H<sub>6</sub> radical complex, as well as the D<sub>2</sub>O-OD complex. An example of the spectra for the VUV co-deposition of H<sub>2</sub>O with C<sub>6</sub>H<sub>6</sub> in Ar and D<sub>2</sub>O with C<sub>6</sub>H<sub>6</sub> in Ar is shown below.



Given the success we had with observing the OH-C<sub>6</sub>H<sub>6</sub> and OD-C<sub>6</sub>H<sub>6</sub> radical complexes in Ar matrices using the VUV photolysis source, we then began working on experiments to produce the OH-C<sub>6</sub>F<sub>6</sub> radical complex, which was one of the radical lone pair-pi complexes I proposed studying for the grant project. In our attempt to produce the OH-C<sub>6</sub>F<sub>6</sub> radical complex, we performed a series of co-deposition experiments with H<sub>2</sub>O and C<sub>6</sub>F<sub>6</sub> in Ar matrix while simultaneously irradiating with the VUV photolysis source. We also performed a series of C<sub>6</sub>F<sub>6</sub>/Ar + VUV deposition experiments as control experiments, in order to determine any peaks that might be due to the photolysis of C<sub>6</sub>F<sub>6</sub> alone. We performed these experiments for approximately one month and unfortunately we were not able to observe any peaks that we could unambiguously assign to the OH-C<sub>6</sub>F<sub>6</sub> radical complex. These experiments were completed at the end of the fall 2018 semester.

During the spring 2019 semester I had four undergraduate students working with me in my research laboratory. During the previous spring, my group had been performing experiments to characterize the H<sub>2</sub>O<sub>2</sub>-C<sub>6</sub>H<sub>6</sub> complex in an Ar matrix at 20 K. In these experiments, we used a solid H<sub>2</sub>O<sub>2</sub>-urea adduct as the source of H<sub>2</sub>O<sub>2</sub> and introduced it into the Ar matrix by flowing gaseous Ar over a glass finger containing the solid H<sub>2</sub>O<sub>2</sub>-urea adduct. We had also synthesized an isotopic hydrogen peroxide-urea sample, which ended up being a mixture of H<sub>2</sub>O<sub>2</sub>-urea, HDO<sub>2</sub>-urea, and D<sub>2</sub>O<sub>2</sub>-urea, with HDO<sub>2</sub>-urea being the deuterium species produced in the largest amount. We redid the isotopic synthesis and were able to obtain a sample in which the D<sub>2</sub>O<sub>2</sub>-urea species was the largest component and so I decided that we would perform a series of experiments using this new isotopic D<sub>2</sub>O<sub>2</sub> with C<sub>6</sub>H<sub>6</sub> and C<sub>6</sub>D<sub>6</sub> to characterize other isotopic variants of the H<sub>2</sub>O<sub>2</sub>-C<sub>6</sub>H<sub>6</sub> complex. The experiments we performed were co-depositions of D<sub>2</sub>O<sub>2</sub> with C<sub>6</sub>H<sub>6</sub>, D<sub>2</sub>O<sub>2</sub> with C<sub>6</sub>D<sub>6</sub>, and H<sub>2</sub>O<sub>2</sub> with C<sub>6</sub>D<sub>6</sub> in Ar matrices at 20 K. Completing these experiments took us until close to the end of the spring 2019 semester. Combined with the experiments we had performed during the previous spring, which were H<sub>2</sub>O<sub>2</sub> with C<sub>6</sub>H<sub>6</sub> and HDO<sub>2</sub> with C<sub>6</sub>H<sub>6</sub>, we have characterized the IR peaks of five isotopic variants of this system in Ar matrices. I presented the work on the full series of isotopic variants of the H<sub>2</sub>O<sub>2</sub>-C<sub>6</sub>H<sub>6</sub> complex at the International Symposium on Molecular Spectroscopy conference in June 2019.

During the summer of 2019, I had one undergraduate student working with me in my laboratory two days per week and I wanted to return to experiments involving a radical-aromatic complex, and given the success with the OH-C<sub>6</sub>H<sub>6</sub> radical complex, I thought we should try to produce a related radical complex, namely the SH-C<sub>6</sub>H<sub>6</sub> radical complex. My thought was that we could use H<sub>2</sub>S and the VUV photolysis source

to produce the SH radical, analogous to how we used H<sub>2</sub>O to produce the OH radical for the OH-C<sub>6</sub>H<sub>6</sub> radical complex experiments. Because we had never used H<sub>2</sub>S in our matrix isolation experiments prior to this, initially we needed to perform some experiments just depositing H<sub>2</sub>S-Ar matrices and then using the VUV photolysis source to produce the SH radical. We spent about one month working on these experiments, which is a little bit longer than normal and this was due to the fact that the H<sub>2</sub>S appeared to be decomposing with time upon sitting in the metal canisters that we use to prepare the H<sub>2</sub>S-Ar mixtures. Eventually we were able to obtain good quality H<sub>2</sub>S-Ar matrices at 15 K and also to obtain Ar matrices that contained the SH radical. We observed a peak at 2612.2 cm<sup>-1</sup> that we assigned to the SH radical in Ar based on a comparison with a previous literature report of the SH radical in Ar, for which the peak was reported at 2607 cm<sup>-1</sup>. We also observed some peaks that are most likely due to the H<sub>2</sub>S-SH complex as well. Once we had a good handle on obtaining SH in an Ar matrix, we began the co-deposition experiments of H<sub>2</sub>S with C<sub>6</sub>H<sub>6</sub> in Ar matrices at 15 K while simultaneously irradiating with the VUV photolysis source. As we have done with other experiments, this involved performing the experiments over a range of concentrations of both of the reagents. Because the SH-C<sub>6</sub>H<sub>6</sub> radical complex is an unknown system, we performed theoretical calculations at the MP2/aug-cc-pVDZ level for the SH-C<sub>6</sub>H<sub>6</sub> radical complex and these predicted that the S-H stretching frequency for the complex should be shifted down approximately 12 cm<sup>-1</sup> from the free SH radical stretch. We examined the S-H stretching region for the H<sub>2</sub>S-C<sub>6</sub>H<sub>6</sub>-Ar + VUV spectra that we obtained to look for a peak that could be assigned to the complex, but unfortunately we were not able to observe any peak that we could unambiguously assign to the SH-C<sub>6</sub>H<sub>6</sub> radical complex. In looking over other regions of the spectra, I noticed a fairly strong peak at 621.0 cm<sup>-1</sup> that was not present when C<sub>6</sub>H<sub>6</sub>-Ar matrices were VUV irradiated without the H<sub>2</sub>S. After doing some literature searching, I discovered that this peak was in good agreement with the most intense peak for the C<sub>6</sub>H<sub>7</sub> radical, which corresponds to a hydrogen atom adding to the C<sub>6</sub>H<sub>6</sub> ring. This radical had been observed previously in solid xenon (*Chem. Phys. Lett.* **2007**, 437, 207) and para-hydrogen (*J. Chem. Phys.* **2012**, 136, 15304) matrices and after careful examination of our spectra, I found nearly all of the other previously reported peaks due to this radical in our Ar matrices. After making this conclusion, I reexamined the spectra from the H<sub>2</sub>O-C<sub>6</sub>H<sub>6</sub>-Ar + VUV experiments that we had performed and discovered that we were also forming the C<sub>6</sub>H<sub>7</sub> radical in those experiments as well, but with a lower yield. In the VUV photolysis of either H<sub>2</sub>O or H<sub>2</sub>S, an H atom is also produced with the OH and HS fragment and the H atom apparently has enough energy to overcome the barrier for the H + C<sub>6</sub>H<sub>6</sub> reaction, which is theoretically predicted to be approximately 10 – 15 kJ/mol. The larger yield from the H<sub>2</sub>S experiments makes sense based on the fact that the H<sub>2</sub>S bond energy is lower than the H<sub>2</sub>O bond energy. Also observed in these experiments is fulvene and benzvalene, which are both isomers of benzene formed from the VUV photolysis of benzene. An example of the C<sub>6</sub>H<sub>7</sub> spectra for the H<sub>2</sub>S-C<sub>6</sub>H<sub>6</sub>-Ar + VUV and H<sub>2</sub>O-C<sub>6</sub>H<sub>6</sub>-Ar + VUV experiments is shown below. While the formation of the C<sub>6</sub>H<sub>7</sub> radical was not the aim of the H<sub>2</sub>S-C<sub>6</sub>H<sub>6</sub>-Ar + VUV experiments, this is an exciting result in that it opens up the possibility of using H<sub>2</sub>S as an H atom source and studying other H atom reactions with aromatic molecules for which the addition radicals have not yet been characterized with IR spectroscopy. To fully confirm the assignment of the C<sub>6</sub>H<sub>7</sub> radical, we still need to perform experiments using C<sub>6</sub>D<sub>6</sub> in order to obtain the HC<sub>6</sub>D<sub>6</sub> radical, which was reported in the previous literature studies. I have three undergraduate students working with me this fall and we will be performing the H<sub>2</sub>S-C<sub>6</sub>D<sub>6</sub>-Ar + VUV experiments over the current fall semester.

I still have one more idea for a way to try to produce the lone pair-pi OH-C<sub>6</sub>F<sub>6</sub> radical complex, which is to try to produce the OH radical by a direct microwave discharge of an H<sub>2</sub>-O<sub>2</sub>-Ar mixture and co-deposition with an un-discharged C<sub>6</sub>F<sub>6</sub>-Ar mixture. We will attempt these experiments sometime over the coming year.

